Integrated Computational Materials Engineering (ICME)

Predictive Tools Development for Low Cost Carbon Fiber for Lightweight Vehicles

- 2020 Annual Merit Review -

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June 3, 2020

Project ID: MAT124

Overview

Timeline

- Start Date: October 1, 2017
- End Date: September 30, 2020
- Percent Complete: 90%

Budget

- *Total* Project Funding: $4,408,032
  - $ 3,000,000 Federal
  - $ 418,032 Cost Share
  - $ 990,000 LightMat Consortium
- *FY 2020* Funding:
  - $ 921,565 Federal
  - $ 140,334 Cost Share
  - $ 330,000 LightMat Consortium

Barriers

- Reduction of vehicle weight necessitates lower-density materials with suitable mechanical properties, low-cost carbon fiber
- Development of a calibrated ICME predictive tool that can identify & optimize fiber processing parameters
- Extend the ICME framework to encompass synthesis and characterization of fibers based on alternative precursors and novel manufacturing processes

Source: 2017 U.S. DRIVE MTT Roadmap Report, Section 3

Partners

- University of Virginia (Lead)
- Pennsylvania State University
- Oak Ridge National Laboratory
- Solvay S.A.
- Oshkosh Corporation

University of Virginia Engineering

Relevance

- **Objective:** To demonstrate carbon fiber (CF) precursor technology and processing techniques capable of achieving the following:
    - Cost ≤ $5/pound
    - Strength ≥ 250 Ksi (1.72 GPa)
    - Modulus ≥ 25 Msi (172 GPa)
    - Strain ≥ 1%
- This objective will be accomplished through the ICME framework, **coupling simulations and targeted experimentation** to evaluate alternative precursors for suitability to manufacture low-cost CF
    - <u>Third year objectives</u> are to conduct scalability studies to predict industrial scale productivity and cost savings with these fibers
    - We are extending lab-scale success with Nylon 6 and ultra-high molecular weight polyethylene (UHMWPE) to <u>pilot production runs</u>
    - We are currently optimizing the conversion of the pilot run fibers <u>to minimize costs</u>
- **Impact** – Achieve significant vehicle weight reduction and develop high-strength materials systems with low-cost carbon fiber
    - Demonstrate a testbed technical framework to enable at-scale production

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Any proposed future work is subject to change based on funding levels.

FY20 Milestones

- The project is on track to meet FY20 milestones

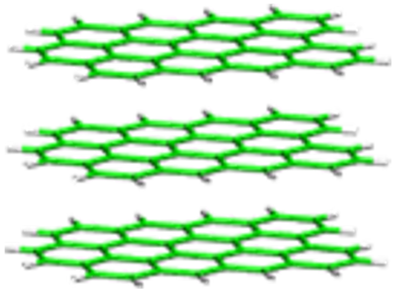
Date	Milestones	Status
September 30, 2019	**FY19 Go/No-Go:** The ICME framework shall identify at least one potential alternative precursor yielding a CF that is projected to meet cost, strength, modulus, and strain requirements	**Met**
September 30, 2020	**M1:** Scalability study of carbon fiber production via optimization of pilot-scale nylon-derived carbon fibers, UHMWPE-derived fibers, and mesophase pitch-derived fibers	**On-Track 70%**
September 30, 2020	**M2:** Experimental validation of carbon fiber properties to quantify the effect of fiber tension, temperature, alternative irradiation treatments (microwave, UV, plasma, *etc.*)	**On-Track 70%**
September 30, 2020	**M3:** Strategic framework for industrial production by polishing the ICME framework with ReaxFF simulations of the nylon/CuCl pretreatment, with targeted design of future precursors for direct carbonization, and with large scale MD and continuum modelling of structure/property relationships	**On-Track 70%**
September 30, 2020	**FY20 Go/No-Go:** Validation of ICME framework to predict the properties of carbon fiber produced via pilot production based on realistic fiber microstructure (porosity, diameter, core/shell, *etc.*)	**On-Track**

- Project end: September 30, 2020

Any proposed future work is subject to change based on funding levels.

Approach

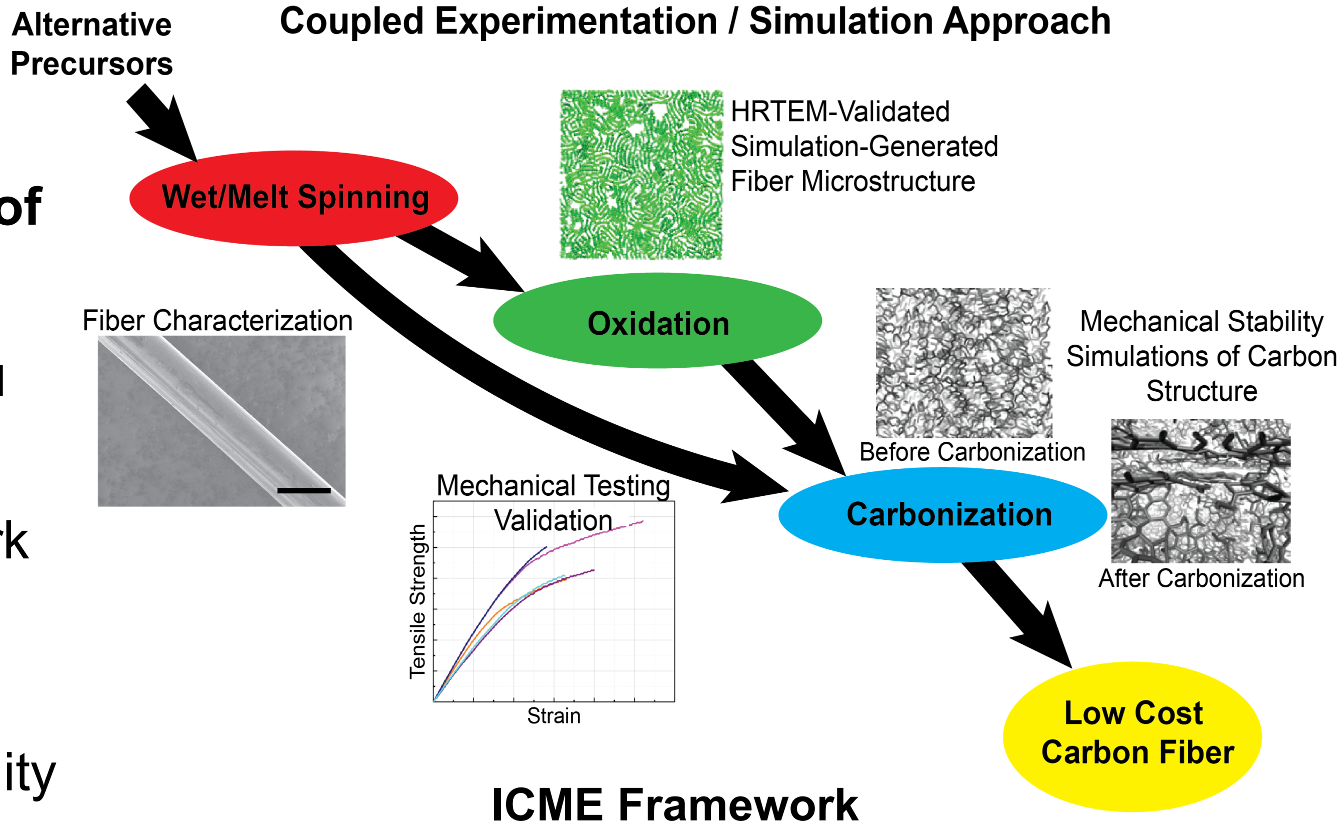
- Our overall objective is to **model conversion of fibers** and **predict properties**
  - Model individual processing steps, including pre-oxidation, oxidation, carbonization, to predict coupled thermal-chemical-mechanical fiber transformation
  - Identify **low-cost alternative precursors** to PAN
- **Closed loop validation** of modeling framework with experimentation
  - Mirror models with mechanical testing and chemical characterization of fibers before and after each step
- **Conduct pilot-production** to evaluate feasibility of scaling fiber production up from lab-scale results
  - Lab conversion procedures need to be optimized at different production scales



Key ICME Objective:
Translate precursor chemical structure to carbon fiber and predict CF properties

Any proposed future work is subject to change based on funding levels.

Coupled Experimentation / Simulation Approach



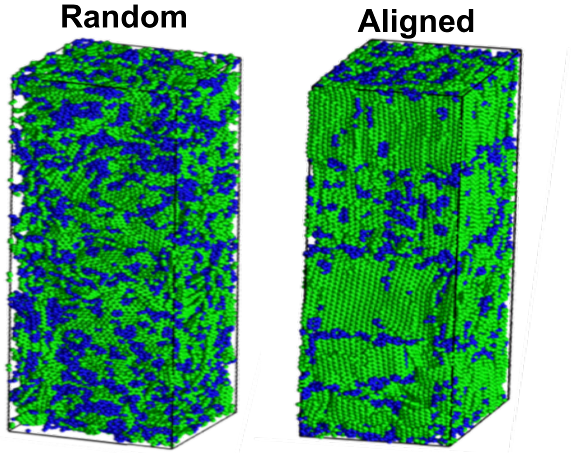
ICME Framework

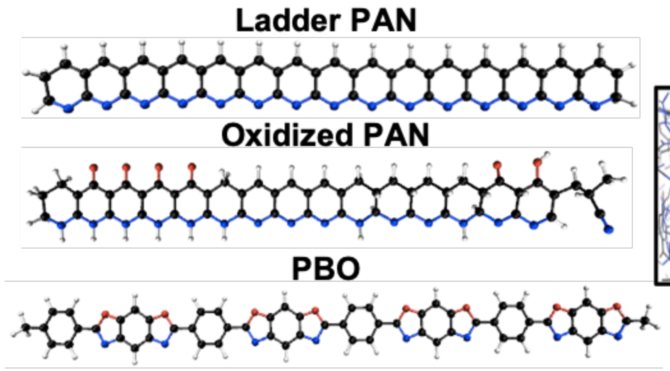
- **ReaxFF simulations** probe the effect of temperature, heat rates, fiber tension, *etc*. on resultant **fiber chemical structures**
- Resulting structure provides input to MD simulations of fiber mechanics
- **MD and continuum FE simulations** translate chemical structure to realistic fiber microstructure and properties, validated against experimental results

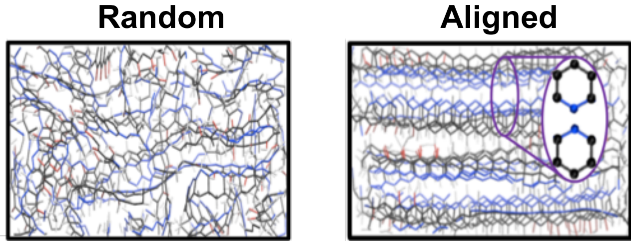
Technical Accomplishments – Year 1

- In **FY18 (Year 1)**, we established and validated the ICME framework with PAN-based fibers
- Under the ICME framework, ReaxFF simulations predict the chemical structure, which is input into MD/continuum FE models to predict mechanical properties

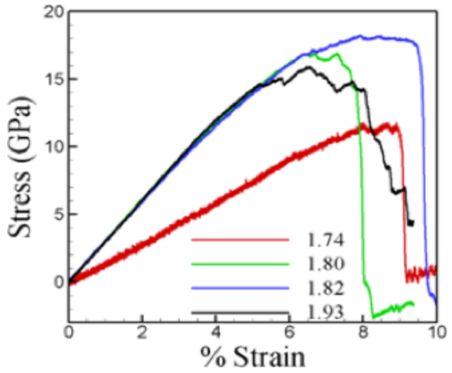
Mechanics Model Polymer Alignment

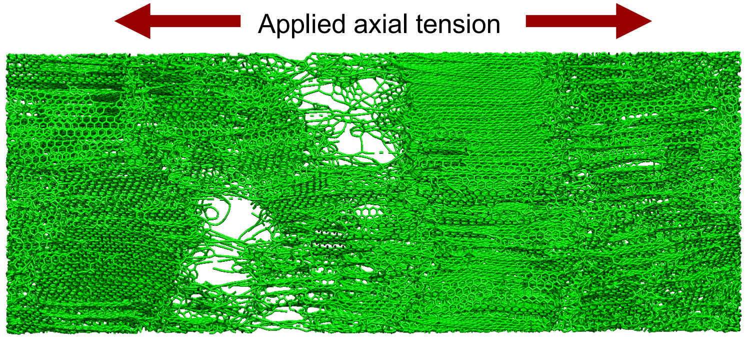




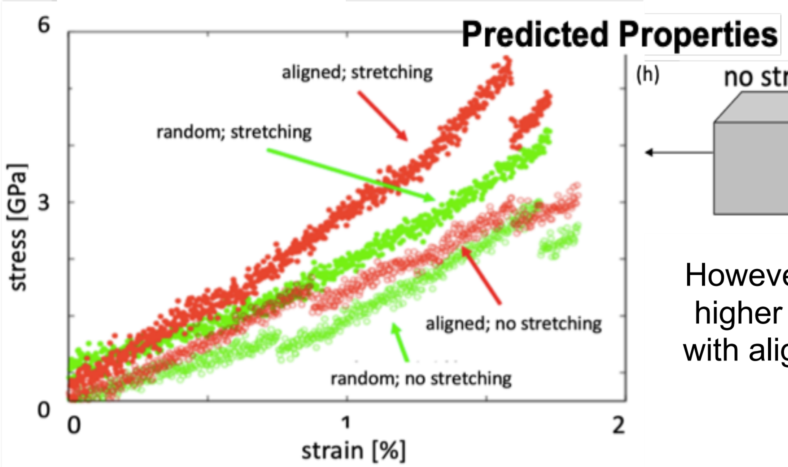


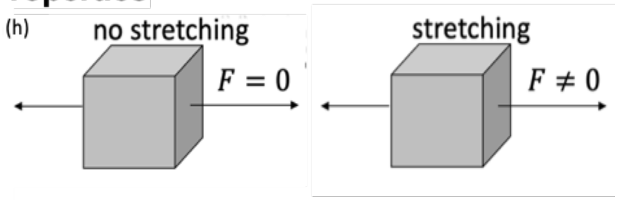
ReaxFF simulations show alignment of the polymers is no detriment to the ring production (PSU).



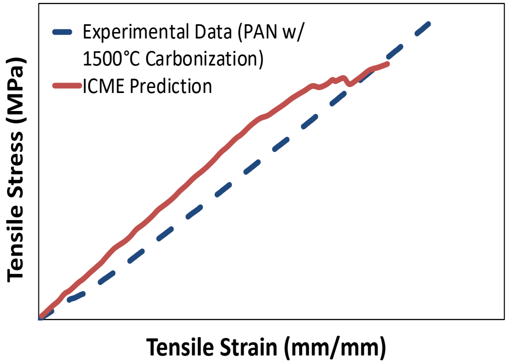


Large-scale MD simulations provide predictions of critical fiber mechanical properties for comparison with lab/pilot-scale production (UVA).





However, these simulations predict higher strength in stretched fibers with aligned polymer chains (PSU).



	Experimental Measurement	ICME Prediction	Percent Difference
Strength	3827 ± 88 MPa	4203 MPa	9.8 %
Strain	1.54 ± 0.003 %	1.71 %	12.9 %
Modulus	276 ± 5 GPa	297 GPa	7.6 %

Final ICME predictions and experimental measurements for PAN-based fiber.

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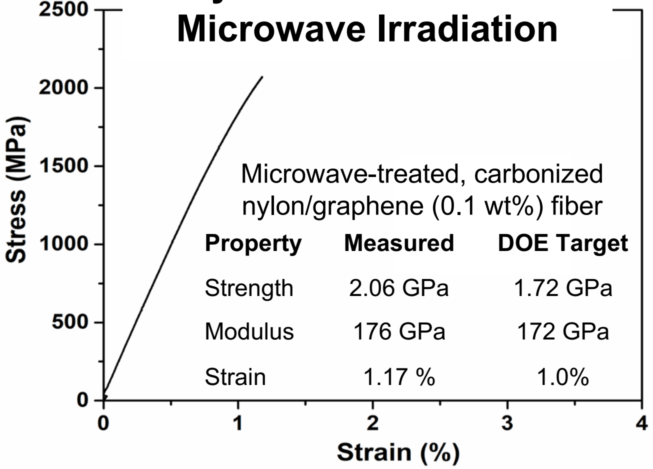
Technical Accomplishments – Year 2

- In **FY19 (Year 2)**, we extended the ICME framework to alternative precursors and non-ideal microstructures
- We considered PBO, Nylon 6, ultra-high molecular weight polyethylene (UHMWPE), and blends/hybrids of these

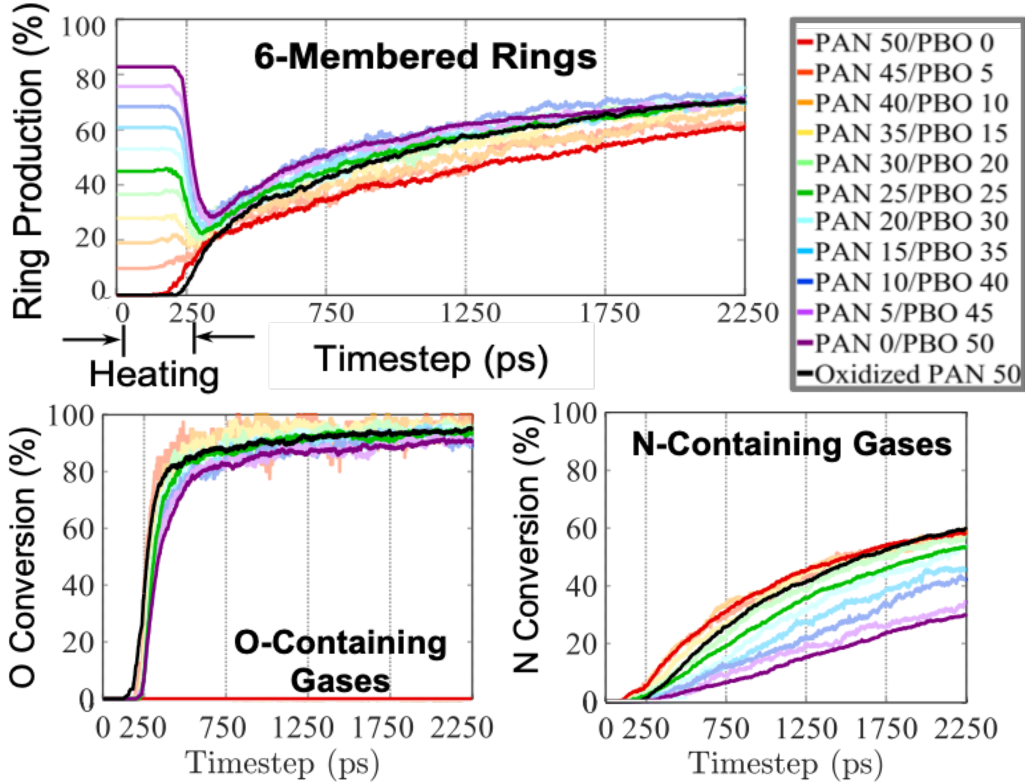
Preliminary Success with Nylon Precursor and Microwave Irradiation



(Left) Lab-scale conversion of nylon fibers with added graphene and microwave irradiation met our target metrics (UVa).

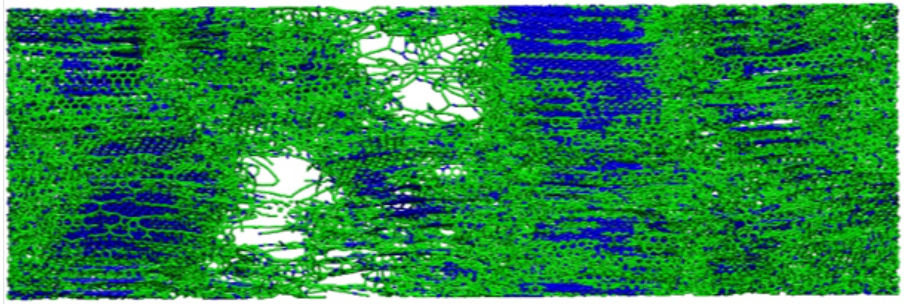
In FY20, we extend these results to a pilot scale!

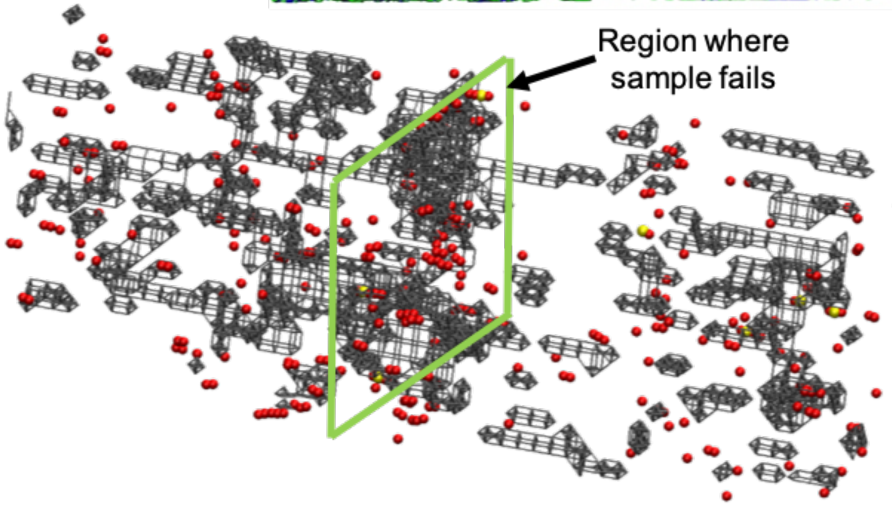
PAN/PBO Blends Normalized Ring Production



ReaxFF simulations of PAN/PBO blends were used to track ring production and gauge the importance of oxygen and nitrogen containing groups to successful fiber conversion (PSU).

3D Fiber Microstructure



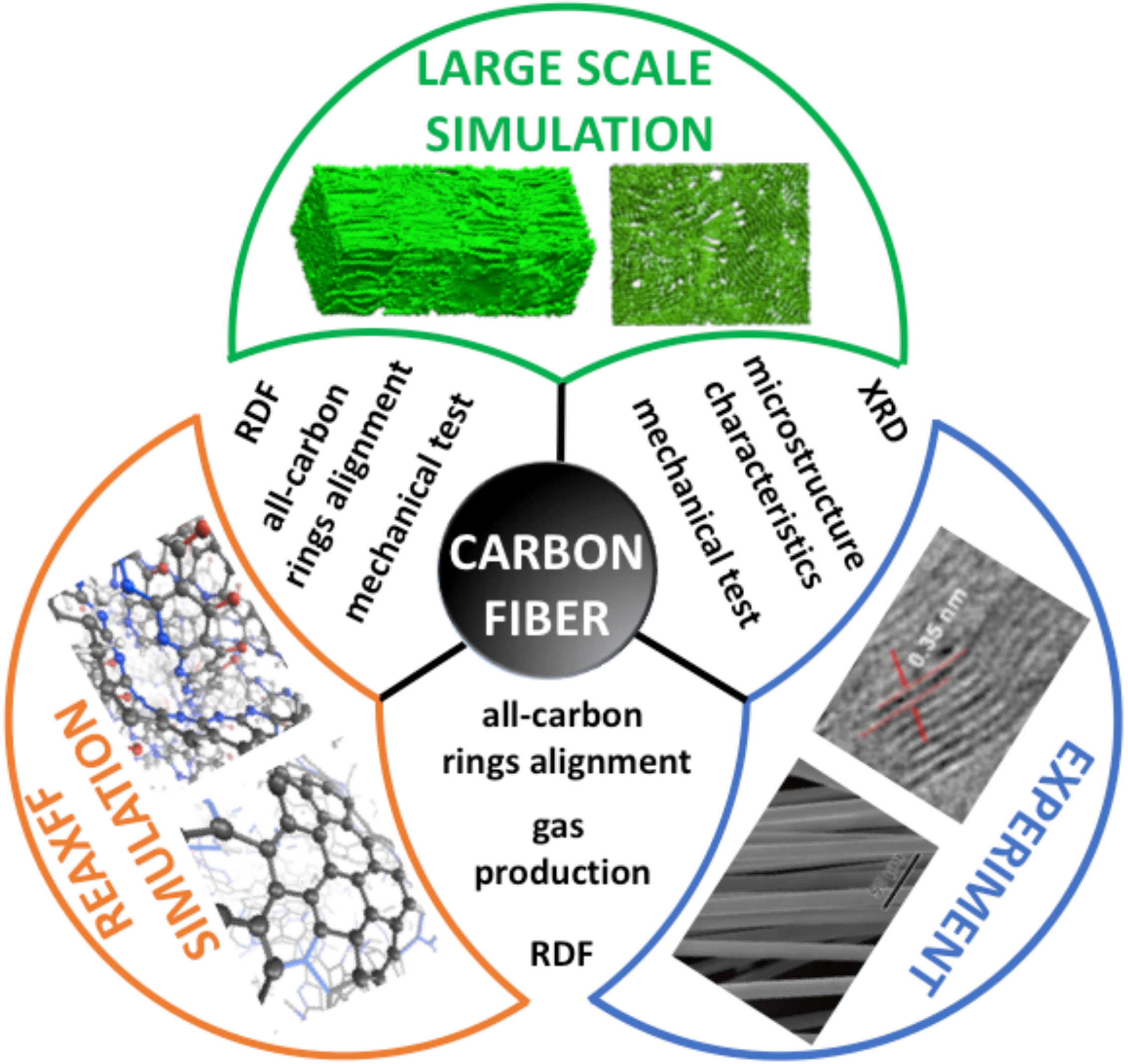


3D Fiber Void Structure

(Left) Voids (gray) within the AIREBO MD simulation were tracked, showing large concentration associated with the location of fracture (UVA).

Technical Accomplishments – Year 3

- In **FY20 (Year 3)**, we applied the ICME framework to optimize the fiber recipes, maximize properties, reduce the time of conversion, and reduce the precursor and conversion costs
- Here, we quickly review our progress with:
  - Ultra-high Molecular Weight PE (UHMWPE)
  - Mesophase Pitch
  - Nylon 6 (melt spun at pilot scale thanks to Solvay S.A. and Hills, Inc.)



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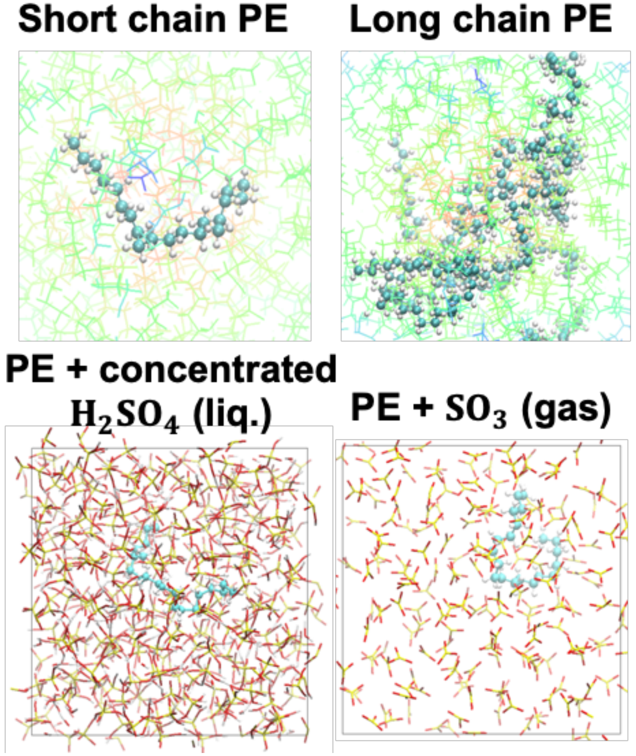
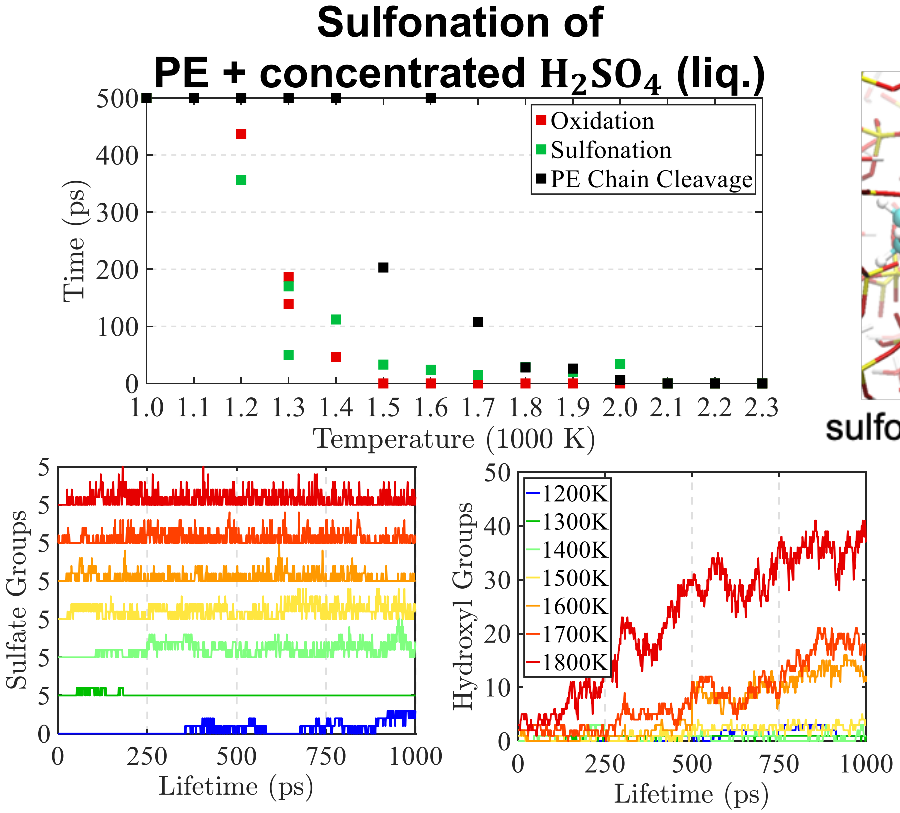
Technical Accomplishments – UHMWPE CF

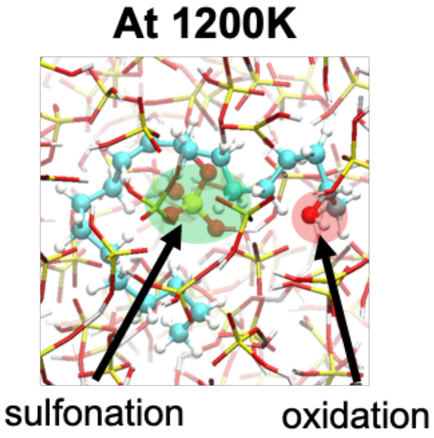
- UHMWPE is converted to carbon fiber via the following steps:
  - Gel spinning
  - Sulfonation at 145 °C for 6 h in H_2SO_4 solution
  - Carbonization at 1200 °C (**No oxidation necessary ➜ lower conversion cost**)
- ReaxFF simulations unveil the chemical reactions and mechanisms of PE sulfonation with (a) concentrated H_2SO_4 and (b) SO_3
  - Sulfate groups, hydroxyl groups, polyolefins, and the breakdown of PE can be observed in both conditions, whereas the sulfonic groups can be only found when PE is sulfonated with SO_3



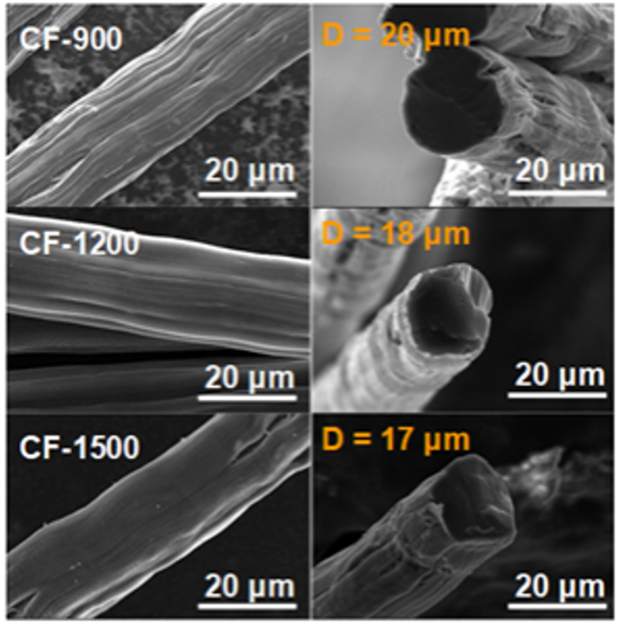
Linear polyethylene structures and the sulfonation reactions as unveiled by ReaxFF-CHONS simulations (PSU).

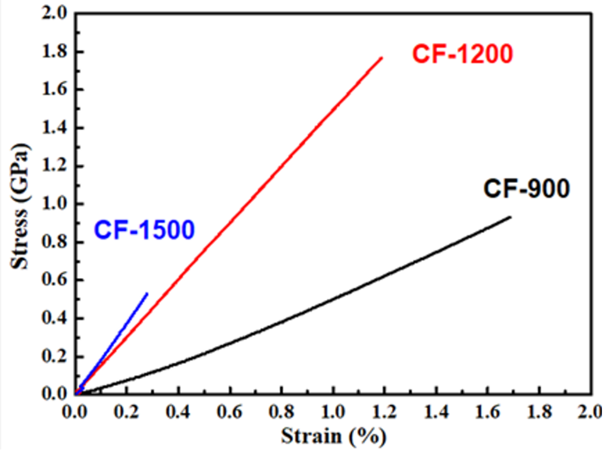


Simulations show the formation of sulfate and hydroxyl groups above 1200K and the breakdown of PE above 1500K (PSU).



Structural formation of sulfate and hydroxyl groups above 1200K (PSU).





Filament tension testing to evaluate optimal carbonization temperature of UHMWPE (UVa).

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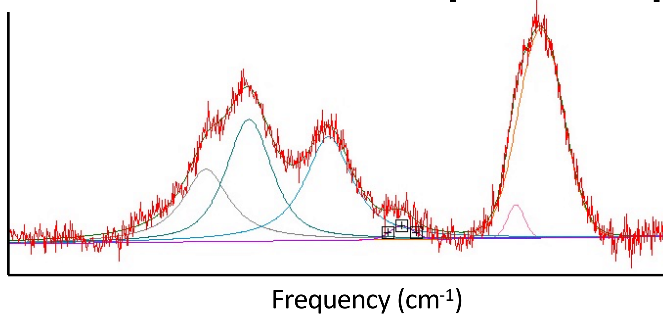
Technical Accomplishments – Pitch CF

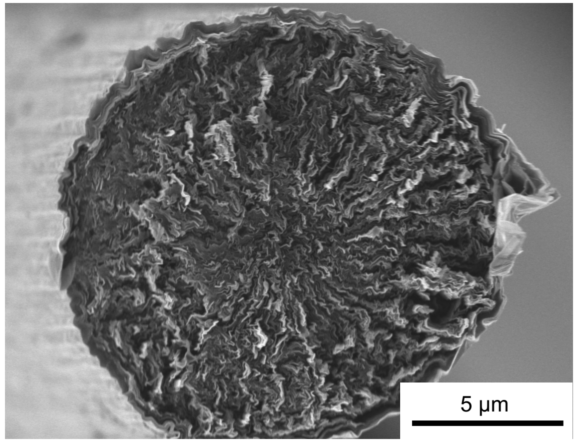
- Pitch is converted to carbon fiber via the following steps:
  - Melt spinning
  - Stabilization at 270 °C
  - Carbonization at 800 to 1200 °C
  - Graphitization at >1500 °C
- A custom spinneret was used to spin fibers with a controlled microstructure to evaluate the effect of structure on fiber performance

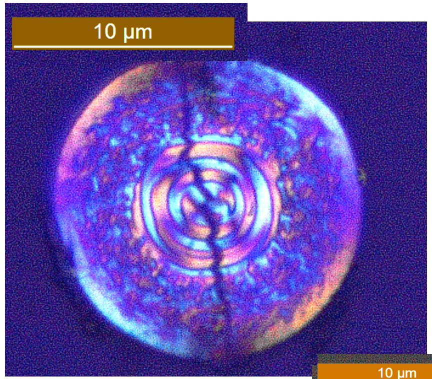
Carbon Fiber Raman Spectroscopy

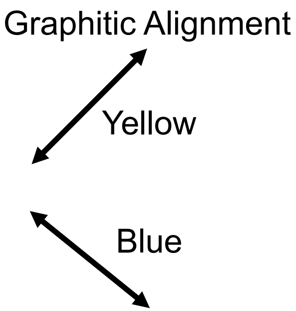


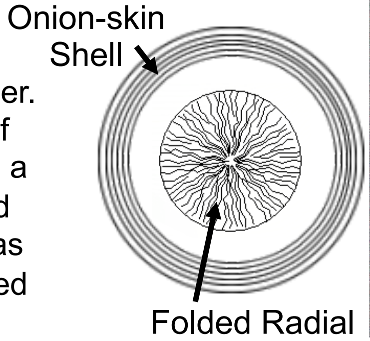
(Above) Sample Raman spectra taken at locations across pitch fiber cross-section (ORNL).

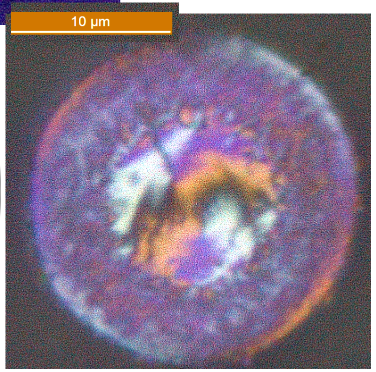
Core-Shell Structure







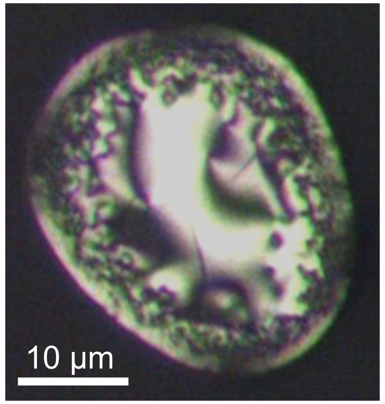




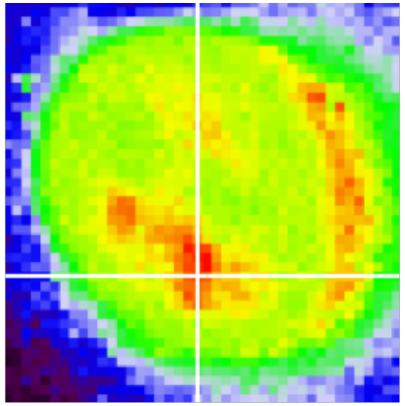
(Above) Electron micrograph of pitch fiber. (Right) Polarized optical micrograph of pitch fiber, showing **internal structure**: a folded radial core, randomly structured middle layer, and onion-skin shell. It was observed that the onion-skin shell helped arrest crack growth (ORNL).

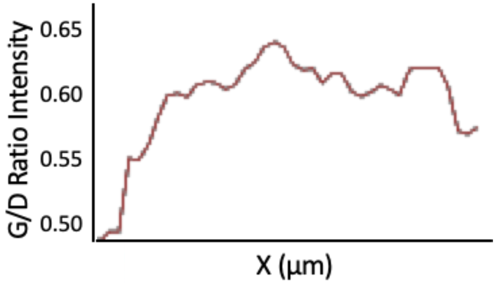
Micro Raman Spectroscopy Characterization

Cross-Polarized Image of Pitch Fiber



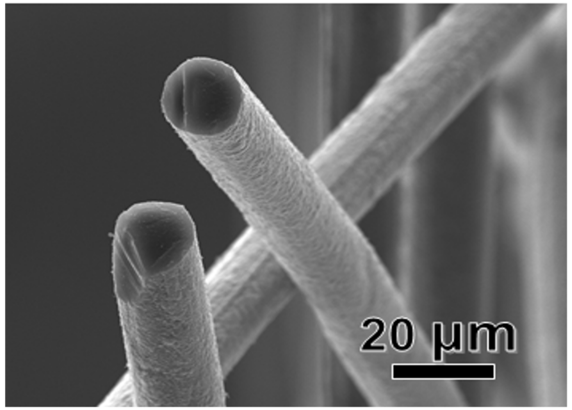
Raman Map of G/D Band Ratio of Pitch Fiber





(Left) Cross-polarized micrograph of pitch fiber. Raman mapping, with 633 nm laser in 1 µm steps through a 50x objective, was performed to map fiber microstructure. Fiber quality was quantified via G band / D band ratio (Right) . We can then begin to **correlate this microstructure to fiber properties** (ORNL).

Technical Accomplishments – Nylon CF

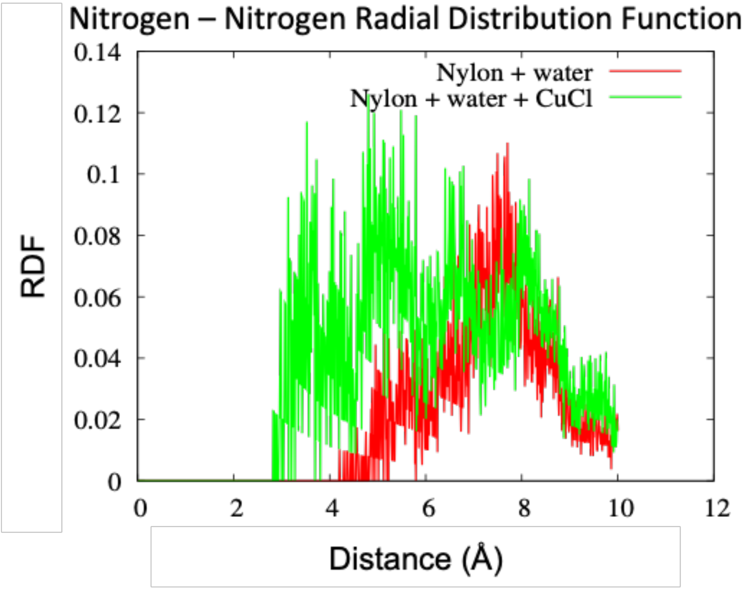


Micrograph of nylon CF (UVa).

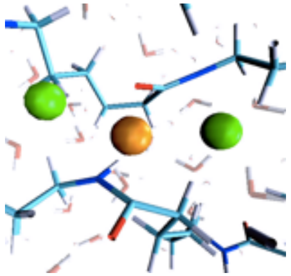
- Nylon is converted to carbon fiber via the following steps:
  - Pre-oxidation in 95 °C CuCl solution for 2 h
  - Oxidation at 200 °C for 25 h
  - Carbonization at 1000 °C for 0.5 h
- We use the ICME framework to inform and optimize each step…

ReaxFF Simulations of CuCl-aided Conversion

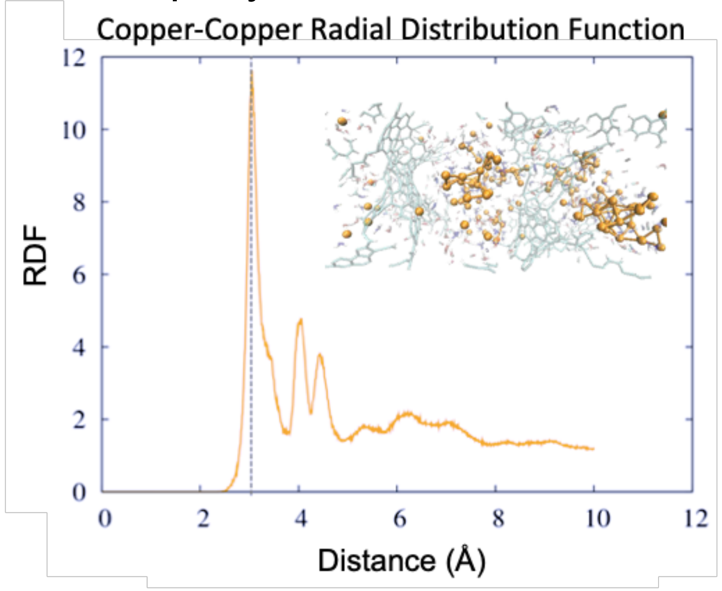
- ReaxFF simulations indicate the presence of metal ions affect nylon chain proximity and fiber thermal response
- Through carbonization, copper clusters evolve and accompany an increase of 6-membered ring production



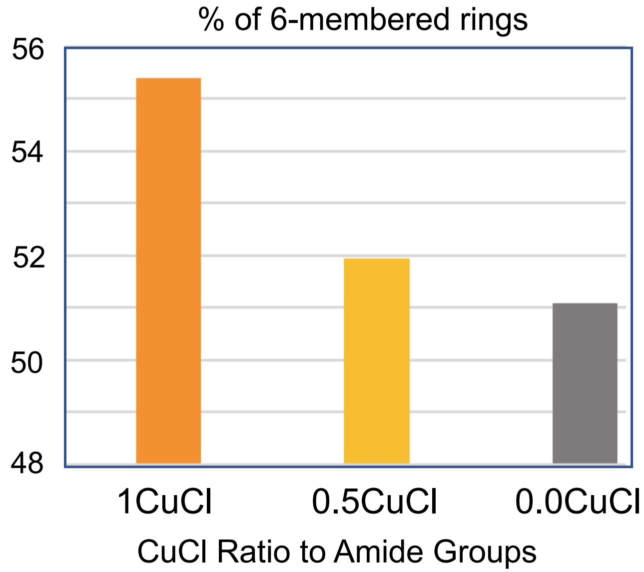
The nitrogen RDF shifts to smaller distances in the presence of metal ions suggests that ions interact with amide groups and affect polymer chain proximity and configuration (PSU).



ReaxFF simulations have revealed one Cu ion can coordinate with two O atoms and two Cl ions (PSU).



The Cu ions RDF after 500ps of carbonization simulation at 2800K followed by a short simulation at 300K. A peak at ~3Å, indicates copper atoms clustering but not yet crystallization (PSU).

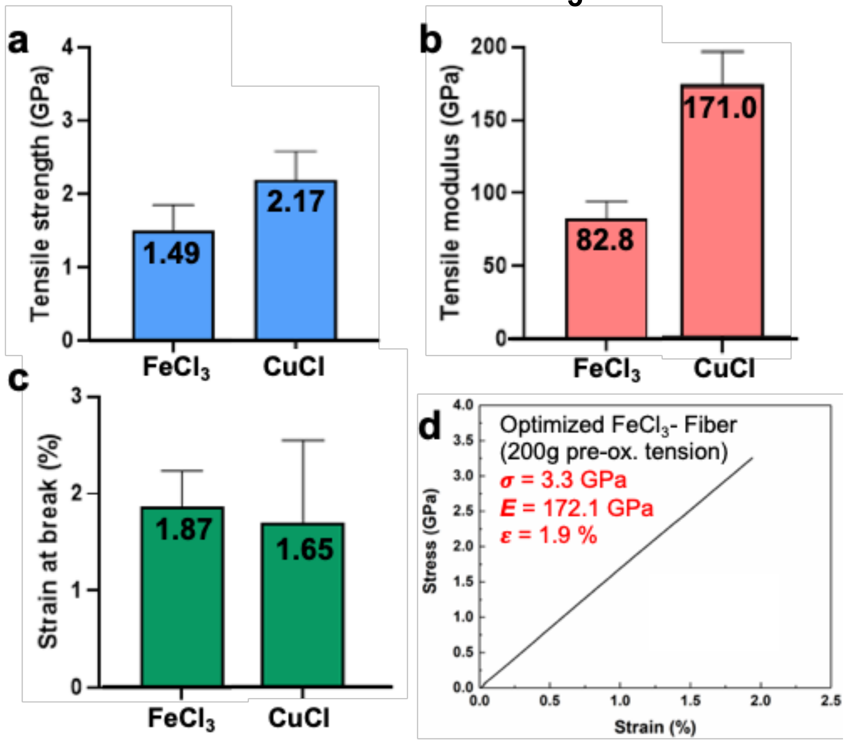


The effect of CuCl ions on the 6-membered ring production for different concentrations of CuCl per each amide group (PSU).

Technical Accomplishments – Nylon CF

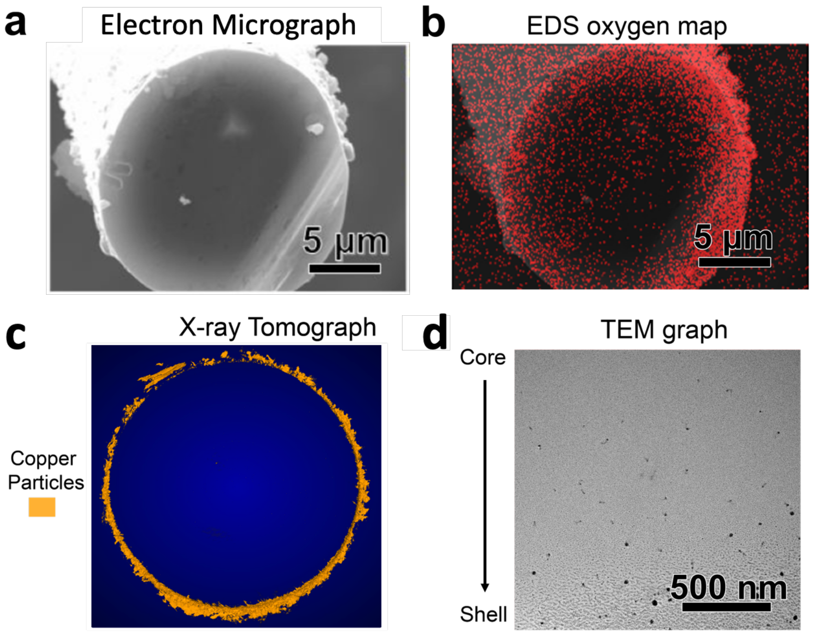
- ReaxFF simulations show role of CuCl in the pre-oxidation of nylon
- Experiments continue this work; can we identify a low-cost, more effective pre-oxidation metal ion alternative to CuCl?
- Experiments are also used to explore other structural effects… Applied tension, fiber diameter, *etc*.

CuCl vs. $FeCl_3$



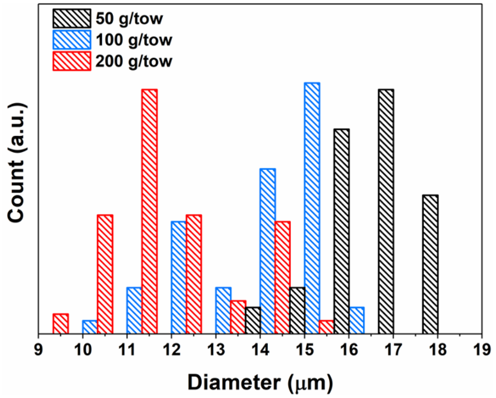
A comparison of CuCl and low cost $FeCl_3$ pre-oxidation treatments (**with 100g of tension**) and effect on (a) strength, (b) modulus, and (c) strain. (d) An optimized $FeCl_3$ treated nylon fiber prepared **with 200g of tension** during pre-oxidation can meet all mechanical property target metrics (UVa).

Metal Particle Diffusion and Oxidation

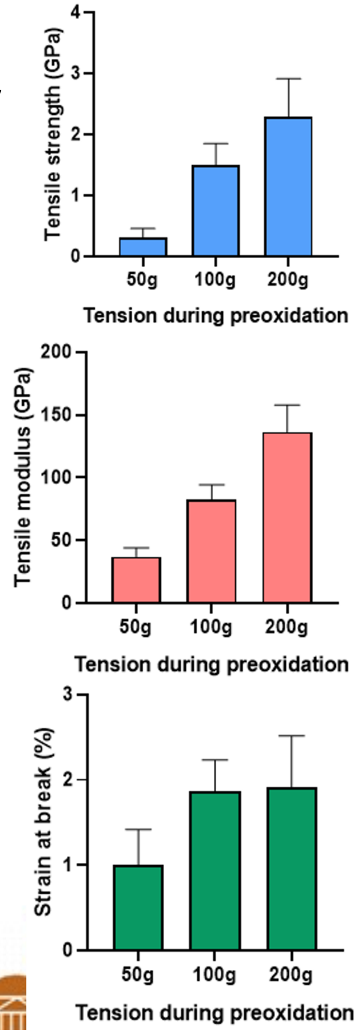


Due to diffusion of oxygen and metal (Cu or Fe) particles, the fibers possess a **core-shell structure**. Shown here, (a) SEM and (b) EDS mapping of oxygen diffusion and (c) X-ray tomography (Brookhaven Nat. Lab.) and (d) TEM mapping of Cu diffusion (UVa).

Optimizing Tension to Decrease Fiber Diameter



We optimize the **applied tension during conversion** to maximize properties and reduce fiber diameter. Shown here, three-levels of tension during pre-oxidation using $FeCl_3$ of nylon CF (UVa).



We aim to reduce fiber diameter to increase this "shell" across the entire diameter.

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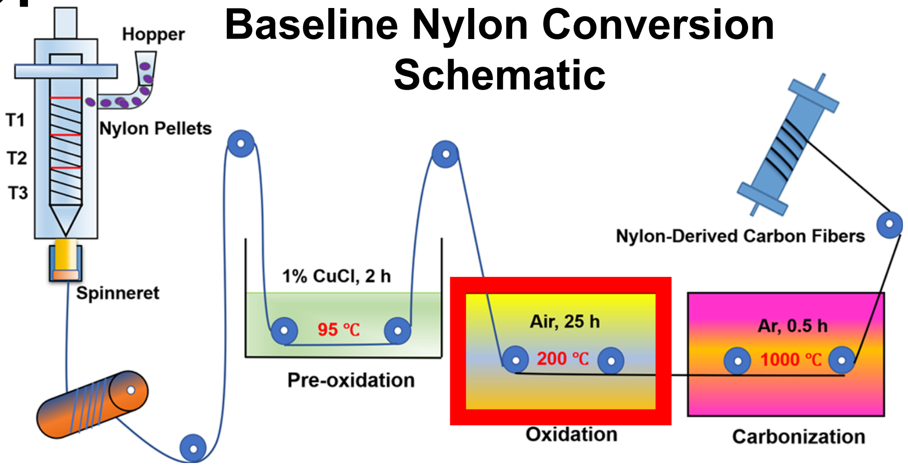
Technical Accomplishments – Nylon CF

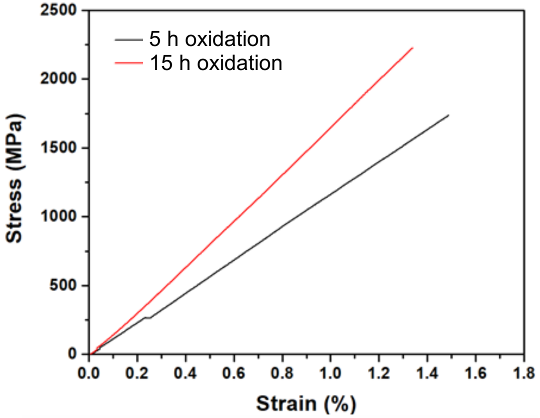
- A critical task is to reduce the baseline 25 h oxidation as low as possible (target 2 h as identified by Solvay)
- We are exploring microwave and UV irradiation
- In the remaining time, we will also explore atmospheric plasma oxidation with ORNL (Felix Paulauskas) and 4M

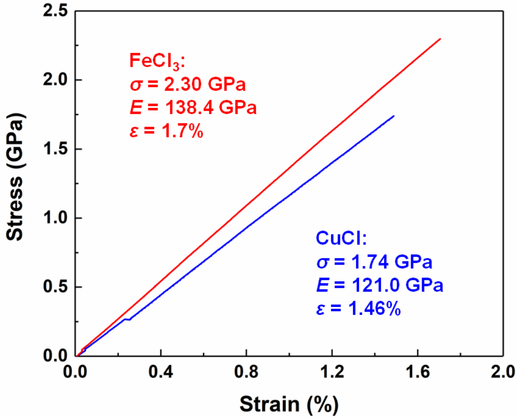
Baseline Nylon Conversion Schematic



Microwave and UV Irradiation

- In the conversion of pilot-scale Nylon fibers, we have achieved a 5 h oxidation (left) with microwave treatments
- We are shortening this oxidation period further to 2 h and even less



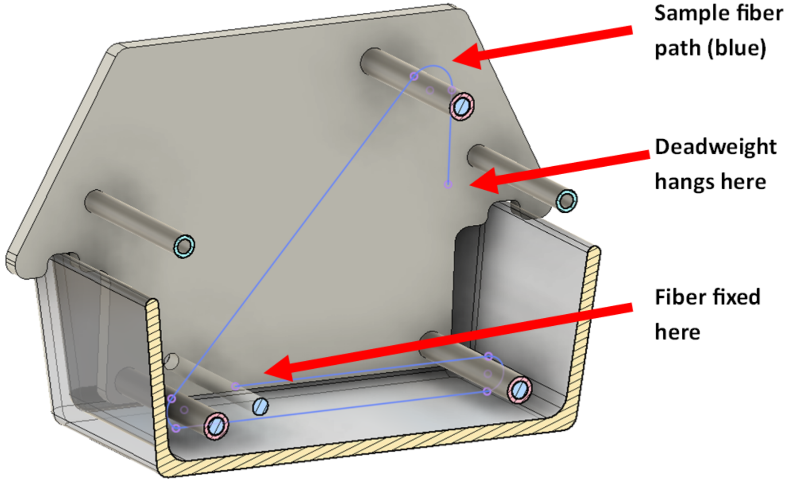


Nylon CF stress-strain curves prepared with microwave irradiation and 5 h oxidation (UVa).

Metrics	Lab-scale: Nylon/PVA/G Microwave+ 5h Ox	Lab-scale: Nylon/PVA/G Microwave+ UV+4h Ox	Pilot-scale: Nylon Microwave +15h Ox	Pilot-scale: Nylon Microwave +5h Ox
Strength (GPa)	2.14	1.78	2.23	1.74
Modulus (GPa)	181	184	174	121
Strain (%)	1.18	0.98	1.32	1.32

Lab-scale conversion was optimized to reduce oxidation of nylon down to 4 h with microwave and UV treatments. We are continuing to optimize the pilot-produced nylon by controlling fiber tension and diameter (UVa).

Microwave Tensioning System



We are developing an *in-situ* microwave tensioning system to optimize the microwave irradiation treatment and maximize properties (UVa).

Any proposed future work is subject to change based on funding levels.

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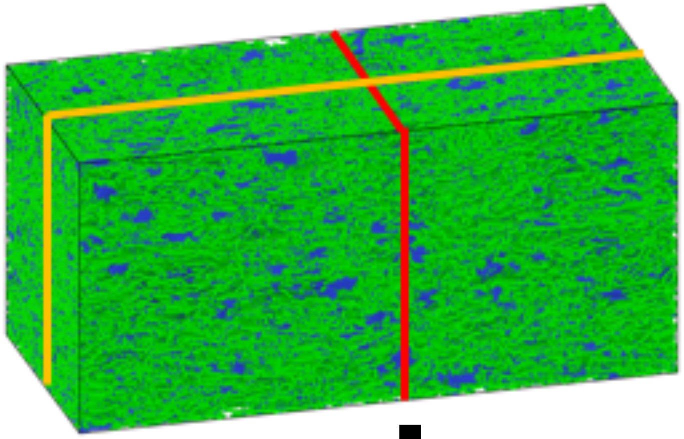
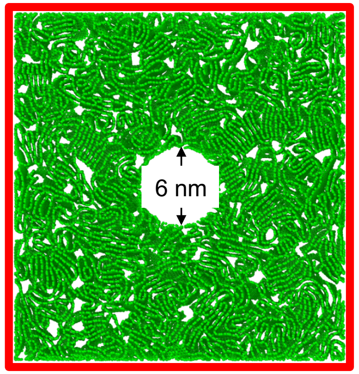
Technical Accomplishments – ICME Predictions

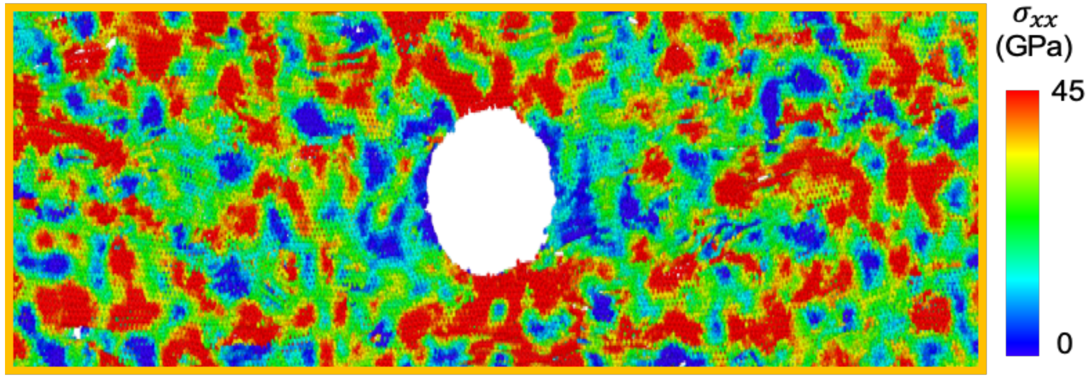
- Atomistic simulations overestimate strength and strain
- To integrate the effect of fiber defects (porosity, inclusions), multiscale atomistic and continuum simulations investigate the effect of nanopores on stress concentration and mechanical properties

Large-scale CF atomistic model, ~3 million atoms (graphitic carbon is colored blue)



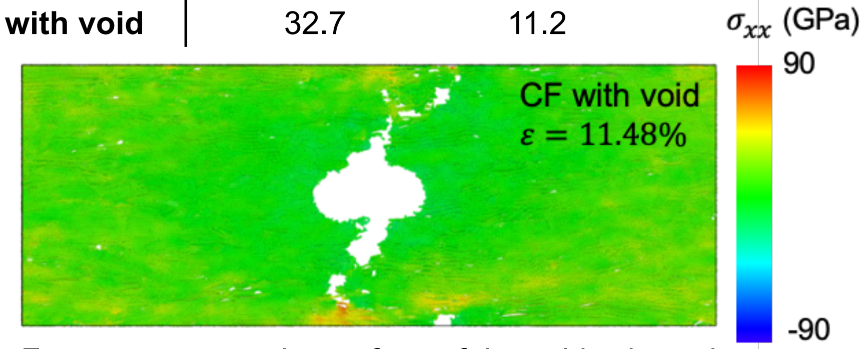
nanovoid with diameter of 6 nm is created at the center



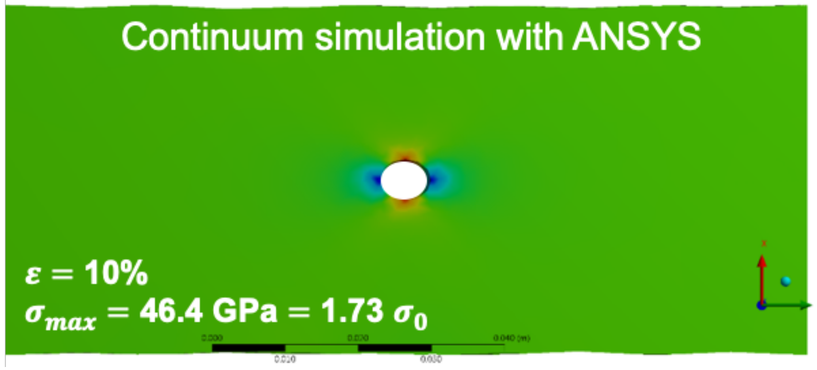


Stress distribution in atomistic MD simulations at $\varepsilon = 10\%$ (UVa).

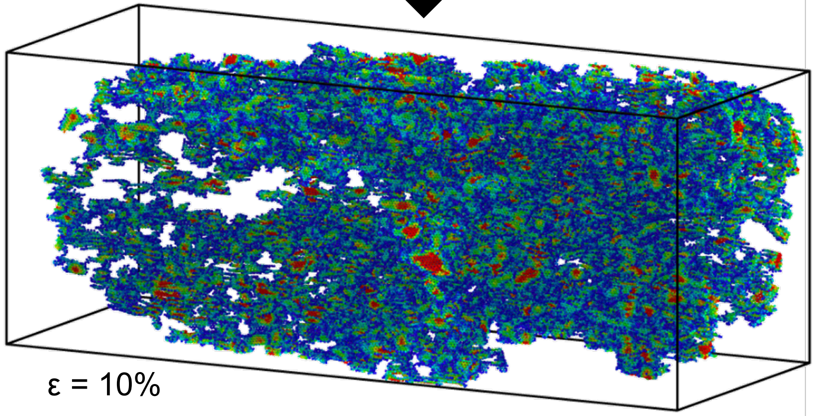
	Strength (GPa)	Strain (%)
CF without void	34.6	11.9
CF with void	32.7	11.2



Fracture starts at the surface of the void, where the stress is locally concentrated. The yield strength decreases in the CF containing the void (UVa).



The stress concentration around pores is explored at relevant scales with continuum finite element modeling. These stress concentrations agree with MD results (UVa).



Mechanical properties are defined by the development of percolating cluster of high stress: $\sigma_{xx} \geq 39.5$ GPa

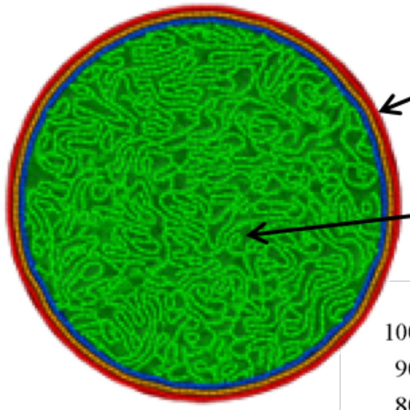
In the remainder of FY20, we will update continuum modeling for variations of pore sizes, geometries, orientations, *etc*. to refine the predicted properties.

Technical Accomplishments – ICME Predictions

- Atomistic modeling of idealized, scaled-down model of a core-shell fiber is used to explore the deformation mechanisms of fiber microstructure and inform continuum modeling
- We can compare MD and continuum models on a nanoscale then scale up the continuum model to relevant fiber length scales with realistic core-shell size fraction

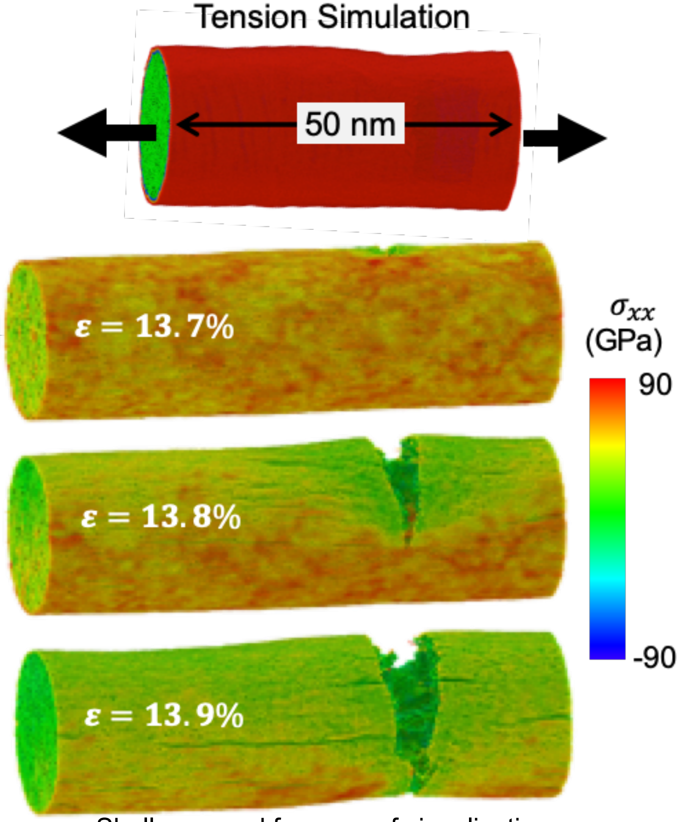
MD Investigation of Core-Shell Structure of Nanofibers

Carbon nanofiber (CNF) with diameter of 20 nm



graphitic 3-layer CNF shell (blue, orange, red)

randomly oriented turbostratic/graphitic core (green)



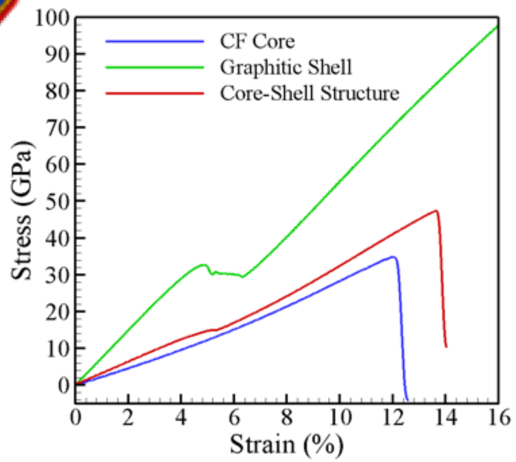
Shell removed for ease of visualization.

Stress-strain curves from 3 systems:

CNF without shell

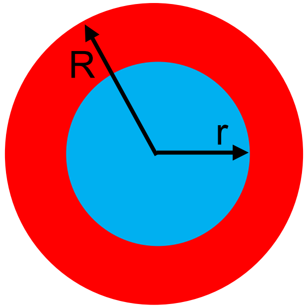
Graphitic shell alone

Core-shell CNF



Nanoscale MD simulations demonstrate fracture initiates at the core-shell interface then propagates through the core. The presence of the shell increases the fiber strength and Young's modulus (UVa).

Continuum Model of Core-Shell CF to Determine Mechanical Properties



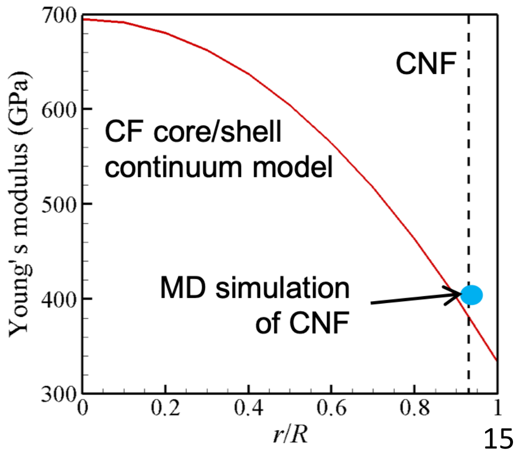
Blue: CF Core
Red: Onion Skin

Strengthening effect of the graphitic shell is quantified by a simple model based on (Kobayashi *et al.*, *Carbon* **49**, 1646, 2011)

$$\pi R^2 \sigma = \pi (R^2 - r^2)\sigma_{skin} + \pi r^2 \sigma_{core}$$

$$\sigma = \underbrace{\left(1 - \frac{r^2}{R^2}\right)}_{b'} \sigma_{skin} + \frac{r^2}{R^2}\sigma_{core}$$

$$\varepsilon = \varepsilon_{skin} = \varepsilon_{core} \Longrightarrow E = b' E_{skin} + (1 - b')E_{core}$$



E_{shell} and E_{core} are calculated from the green and blue MD stress-strain curves; thus, we can predict the E_{CF} at an equivalent scale. Now, we will extrapolate these predictions to parameters of experimental CF (UVa).

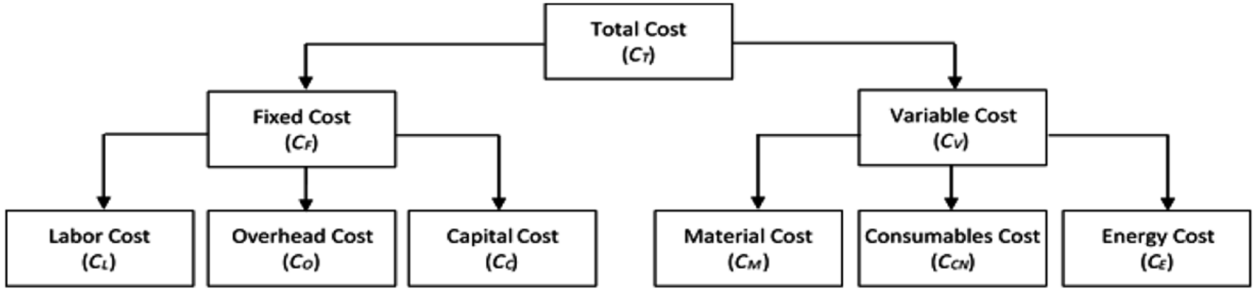
Technical Accomplishments – Year 3

- From this work, we have thus far achieved the following properties towards our target metrics

Metrics	DOE Target	UHMWPE	Pitch	Nylon (Lab-scale, 4-h ox)	Nylon (Pilot-scale, 15-h ox)
Strength (GPa)	1.72	1.77	0.71	1.78	2.23
Modulus (GPa)	172	179	440	184	174
Strain (%)	1.0	1.19	0.6	0.98	1.32
Precursor Cost ($/lb)	-	1 – 2.2	1-2.5	0.5 - 2	
Total Cost ($/lb)	5	4.1 – 5.5	5.4 – 7.3	3.3 – 5.3 (assumes 2 h oxidation)	

- Mechanical properties determined by uniaxial, single filament tension testing
- Precursor costs based on market prices
- Total costs were predicted by extending conversion costs for PAN to relevant time scales for alternative precursor conversion
- *To achieve a total cost of 3.3 – 5.3 $/lb for nylon CFs, we need to reduce oxidation down to at least 2 h*

(Right) Gill, *et al.*, Cost Estimation Model for PAN Based Carbon Fiber Manufacturing Process, 2016.



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Response to Reviewer Comments

- *We thank the reviewers for their previous helpful comments*
- "What assumptions underly the simulations? [Are] perfect atomic/molecular structures are assumed?"
  - *Response*: In FY20, we are extending the simulations to non-perfect, realistic structures. ReaxFF simulations quantify the growth of non-perfect carbon rings (*i.e.*, non-6-membered rings) during conversion. MD and continuum simulations are also targeting the effects of core-shell structure and pore size, shape, and distribution.
- "How predictable are [the mechanical properties and cost based] on batch to batch variation?"
  - *Response*: We do see variation of mechanical properties from batch to batch. This variation is reduced (<10%) through implementation of our single filament, off-axis tension characterization system, which helps us align fibers to <1° during tensile testing. The cost may vary with specific conversion steps, such as duration of oxidation.
- "While nylon showed the need for a long oxidation step, the team is looking at ultraviolet (UV) and related ways of reducing the time of oxidation while realizing high post-properties. This has significant implications on cost."
  - *Response*: Based on our projections, we need to achieve a 2-hour oxidation to meet cost targets. However, microwave, UV, and/or plasma treatments will also add costs, so we may need to reduce oxidation <<2 h. We will minimize oxidation by reducing fiber diameter (via fiber tension) and by working with ORNL and 4M to test pilot-scale microwave, UV, and plasma treatments to confirm their cost and effect on oxidation.
- "It was unclear what the carbon yield is from the alternate precursor such as PE and nylon."
  - *Response*: Thermogravimetric analyses have shown carbon yields after conversion of 34.9 % for CuCl-treated nylon CF, 44.2 % for $FeCl_3$-treated nylon CF, and 42.5 % for UHMWPE CF.

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Collaboration and Team Coordination

- **University of Virginia**, PI Li & Co-PI Zhigilei
  - Experimental and statistical analysis of carbon fiber conversion supported by MD and continuum FE simulations
- **Pennsylvania State University**, Co-PI van Duin – Subcontractor
  - Simulations of chemical conversion of precursors into carbon fiber
- **Oak Ridge National Laboratory**, Co-PI Klett – Subcontractor
  - Experimental testing and characterization of alternative precursors
- **Solvay S.A.**, Co-PI Billy Harmon – Subcontractor
  - Industry guidance on fiber characterization and operation of pilot production run of carbon fiber from alternative precursors
- **Oshkosh Corporation**, Co-PI Robert Hathaway – Subcontractor
  - Industry insight on constraints and priorities for technology transfer from research laboratories to industrial production

Remaining Challenges and Barriers

- Challenge: Scalability of fiber microstructure
  - We are investigating the scalability of fiber structure and properties from the lab-scale to pilot-scale. We have found that the fibers are different between lab and pilot scale. Additional steps are included in the preparation of pilot-scale fibers, such as surface treatments and sealants. These treatments change the microstructure and properties; thus, the ICME framework and the specific conversion procedures must be optimized.
- Challenge: Cost predictions of industrial scale production
  - The cost predictions are based on PAN conversion, adjusted for relevant time scales of converting nylon and PE. Large-scale conversion has not been performed before, so it is difficult to predict the costs of that production. Some initial equipment investment would also be required, and we are working with Solvay, Oshkosh, and ORNL to design new equipment to continuous conduct new conversion procedures (CuCl pre-oxidation, microwave irradiation, *etc*.). We are also working with these partners to evaluate the costs of the pilot production run.
- Challenge: Reduce the oxidation time for nylon
  - A critical task to reduce the cost of CF conversion of nylon is to reduce the oxidation time of nylon, down from 25 h to 2 h or less. To do this, we are adding more tension to reduce the fiber diameter and reduce the time required for oxygen diffusion during oxidation in addition to microwave and UV irradiation treatments to supplement conventional oxidation, as well as atmospheric plasma oxidation.

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Any proposed future work is subject to change based on funding levels.

Proposed Future Research

- This project will end this year in September 30, 2020
- Remaining tasks:
  - To complete scalability / economics study based on pilot production runs
  - Finalize ICME framework with ReaxFF and MD simulations
  - Complete continuum FE model predictions based on experimentally measured pore size and distribution
  - Complete mechanical testing and characterization of pilot-scale alternative fibers to validate ICME predictions

Any proposed future work is subject to change based on funding levels.

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Summary

- We previously **established an ICME framework** to predict fiber properties
- Here, we focus on improving that ICME framework for realistic fiber molecular structure and microstructure
  - **ReaxFF simulations** target the role of metal ions on pre-oxidation treatment of nylon fibers, predict the transformation of PE during sulfonation, and investigate future alternative precursors
  - **Atomistic MD simulations** translate molecular structure to fiber microstructures, and **continuum models** translate mechanical properties to relevant carbon fiber length scales
  - **Experimental testing** validates these conversion mechanisms and unveils new pathways (microwave, UV, *etc*.) to low-cost CF conversion
- We have demonstrated low-cost, high-performance CF from alternative precursors

Metrics	DOE Target	PAN*	UHMWPE	Pitch	Nylon (Lab-scale)	Nylon (Pilot-scale)
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*Gill, *et al*., Cost Estimation Model for PAN Based Carbon Fiber Manufacturing Process, 2016.

- In the remainder of FY20, we will:
  - Complete scalability study based on the pilot production runs
  - Finalize ICME framework with continuum FE model predictions
  - Complete experimental characterization to validate ICME predictions

Any proposed future work is subject to change based on funding levels.

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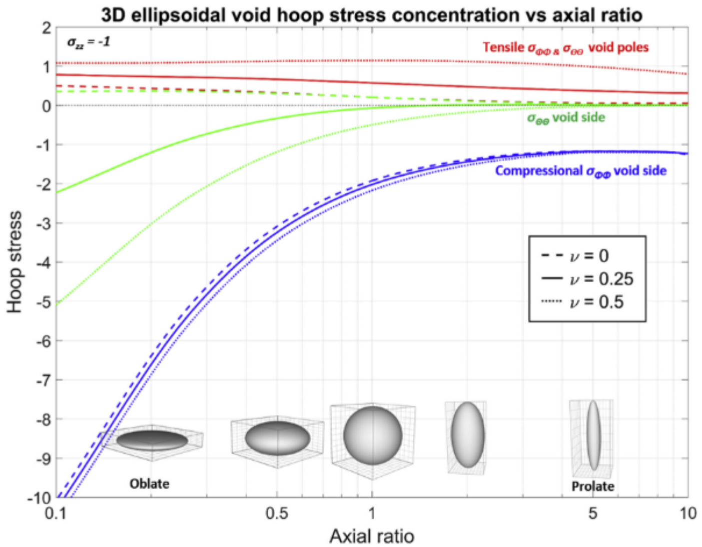
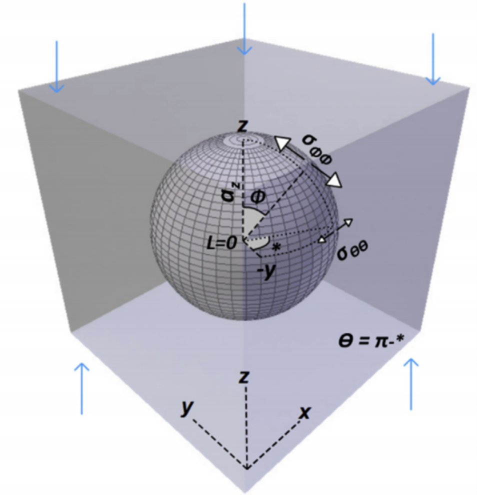
Technical Backup Slides

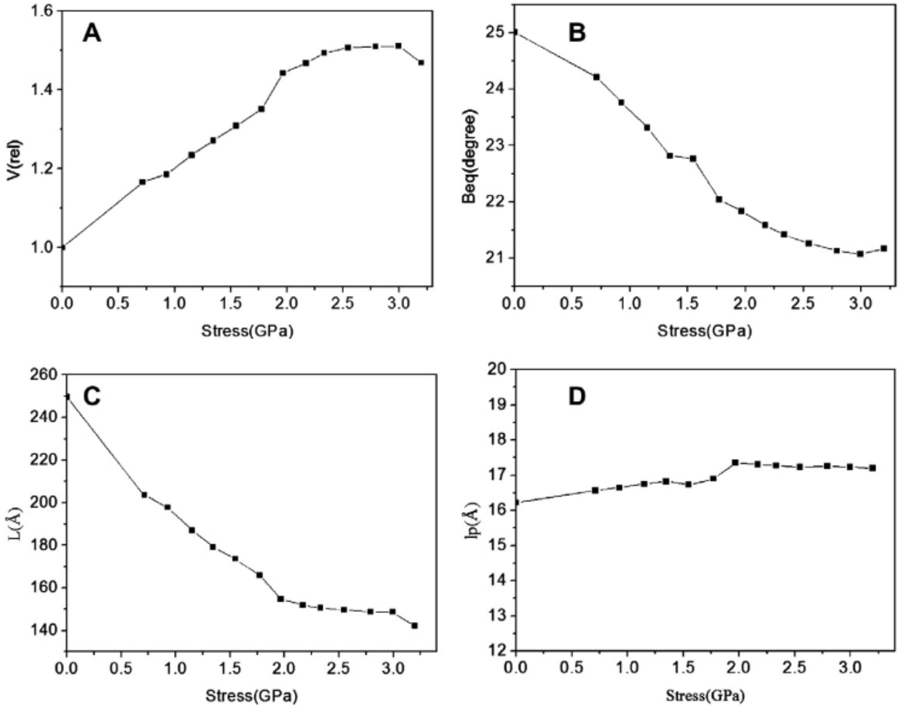
Technical Backup Slides

Experimental Variation of Pore Shape and Size Documented in Literature



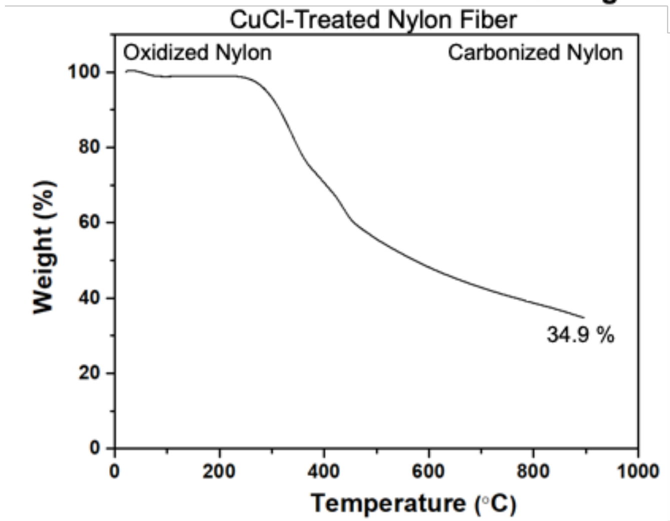


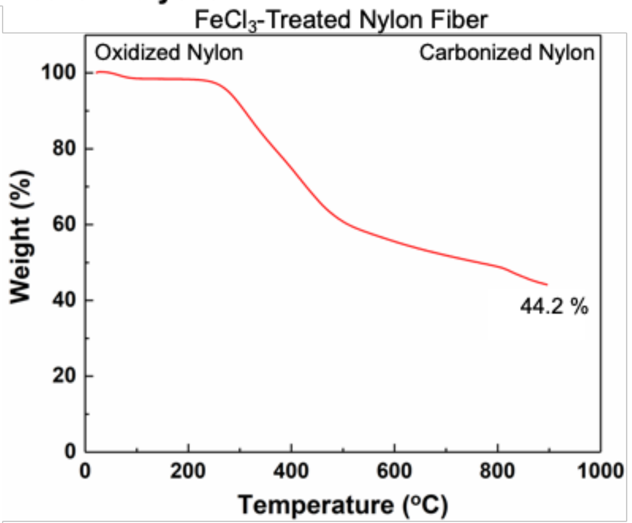
Displacement discontinuity boundary element method (BEM) developed to ascribe geometric properties of voids [T. Davis, *etc. J. Struct. Geol.* **102**, 193-207, 2017].



Shape and size of pores in a bundle of PAN-based carbon fibers measured from synchrotron small angle scattering x-ray scattering (SAXS) during tensile testing [C. Zhu, *et. al. Carbon* **50**, 235-243, 2012].

Thermogravimetric Analyses





(Left) Thermogravimetric analyses of nylon fibers to characterize carbon yield after conversion. The carbon yield increased when conducting pre-oxidation with $FeCl_3$ instead of the more expensive CuCl (UVa).

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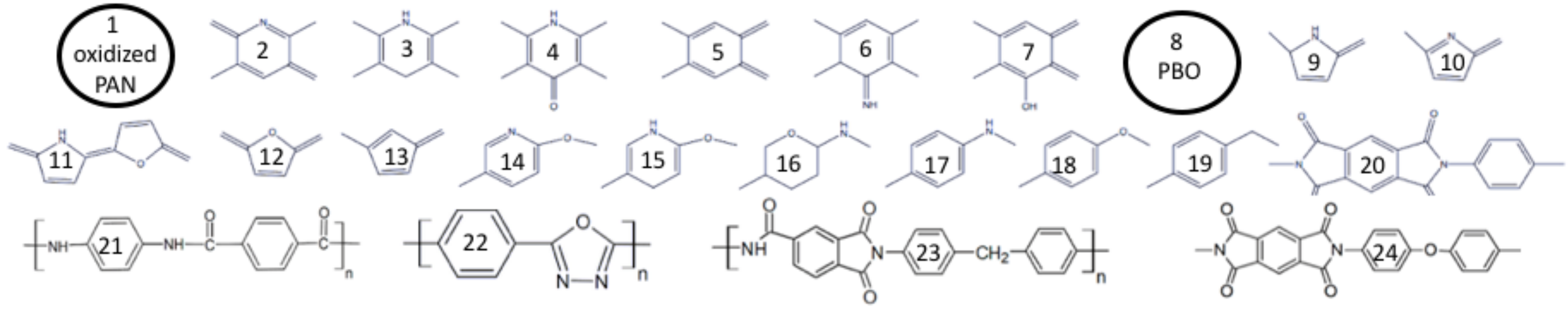
Technical Backup Slides

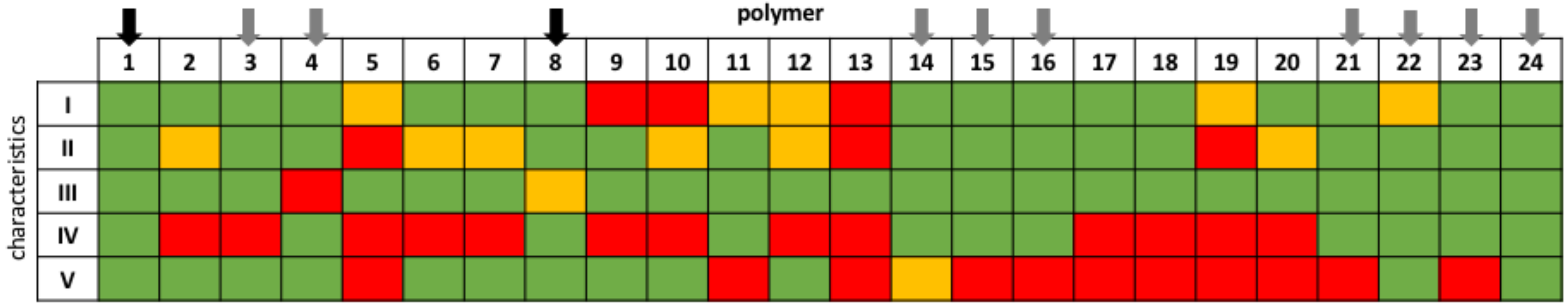
(a)



(b)

	CHARACTERISTICS	meeting the criteria	borderline	not meeting the criteria
I	the higher density of the precursor the better	≥ 1.4	≈ 1.3	≤ 1.4
II	enough carbon atoms, but not too much	$> 40 \text{ and } < 55$	$= 40 \text{ or } = 55$	> 55
III	enough of hydrogen atoms, but not too much	> 22	$= 22$	< 22
IV	Enough of nitrogen and oxygen atoms to facilitate the reactions	> 5	$= 5$	< 5
V	Enough of nitrogen or oxygen atoms, to facilitate the reactions	> 10	$= 10$	< 10

(c)



The black arrows indicate the target systems that can be successfully carbonized; the gray arrows indicate other promising polymer precursors for the direct carbonization

Tested polymers for possible direct carbonization. (a) Schemes of the monomers of all considered polymers. (b) A table with the considered criteria for the polymers benchmarking, to identify the characteristics of the promising precursor for the direct carbonization. (c) A table with the all characteristics categorized if they are meeting or not the chosen criteria (PSU).

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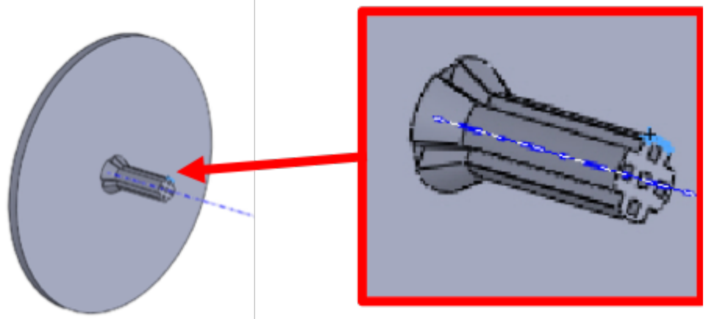
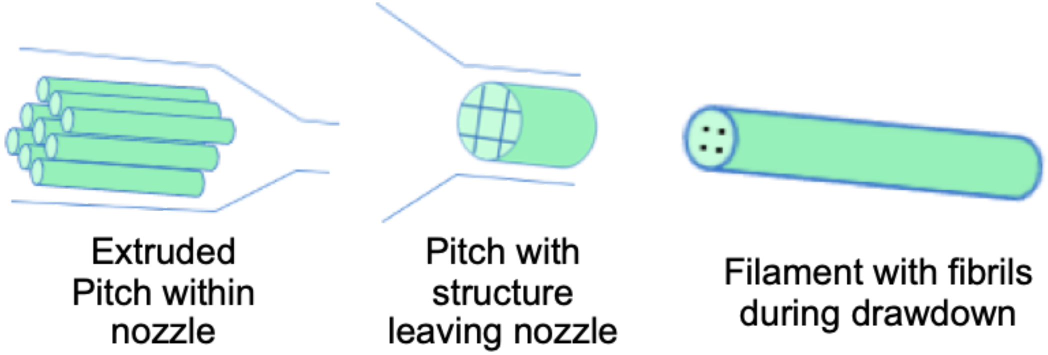
Technical Backup Slides

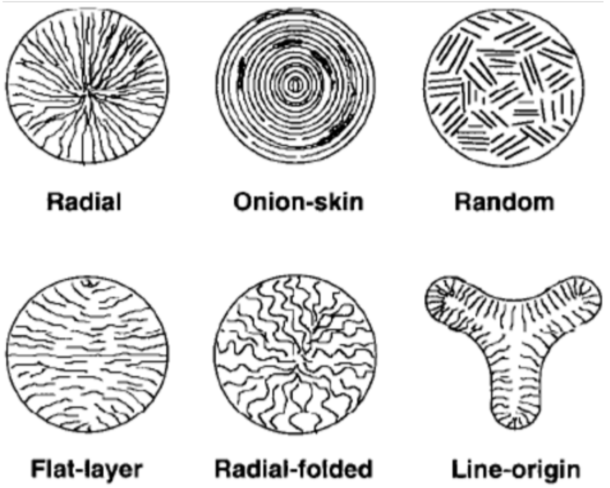
- ORNL is also investigating the role of fiber microstructure on resulting properties using mesophase pitch fibers; this work will inform future fiber structural design

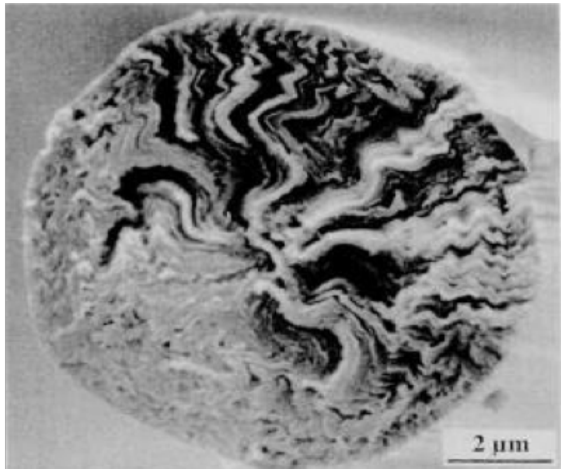


3D printed brass spinneret insert for production of mesophase pitch fibers (ORNL).

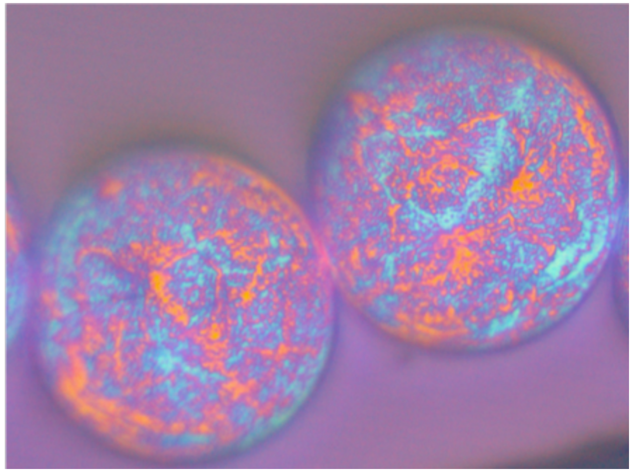


The spinnerets introduces fibrils within the pitch fiber, creating a controlled microstructure, which will be tested to evaluate effect on mechanical properties (ORNL).





(Left) Schematics of documented fiber/graphitic structure observed by Fathollahi and White and (right) SEM of graphitic structure in pitch fiber (J. of Rheology, 1994; Biennial. Conf. on Carbon, San Diego, 1995).



Preliminary polarized light images of first pitch fibers produced via new spinneret indicate new fiber microstructure (ORNL).

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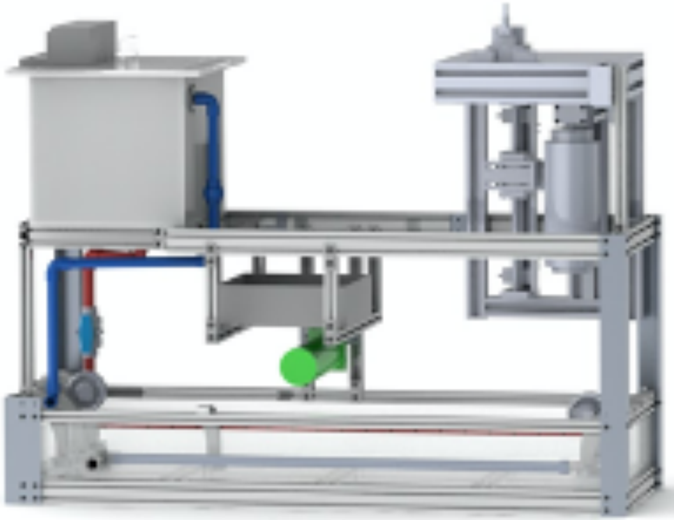
Technical Backup Slides

UVa has assembled customized, modular carbon fiber synthesis stations including:

- A single-filament fiber melt spinning system
  - Interchangeable nozzles (dia. 250 – 500 μm)
  - 3-zone temperature control
  - Up to 4000 m/min take up rate
- Continuous fiber salt bath treatment system
  - Metal salt solution resistant
  - Heated, cross-flow bath up to 80 °C
  - Residence time up to 2 h
  - Adjustable line tension (150 – 500 g)
  - Max package fiber layer thickness of 10 mm
  - Fiber can be rinsed and dried prior to spooling

Continuous Fiber Bath Treatment Station

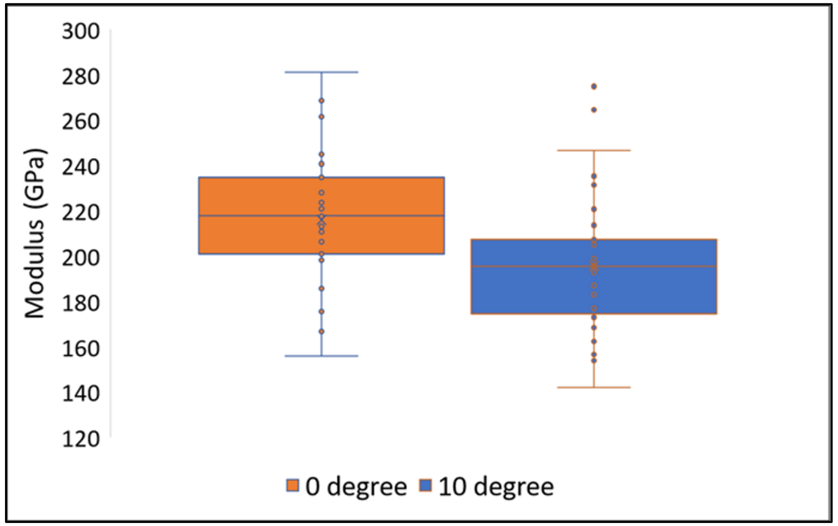


Melt Spinning System with Interchangeable Accessories and Sensors

Any proposed future work is subject to change based on funding levels.

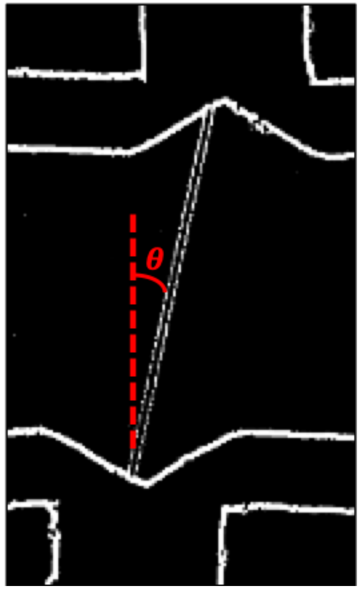
Technical Backup Slides

- UVa has also developed an off-axis single filament monitoring system to ensure tension testing of filaments aligned to <1°
- Commercial fibers with known properties were used to validate the system, demonstrating significant reductions in modulus with increasing off-axis angle
- Forthcoming publication to propose modification to ASTM C1557-20

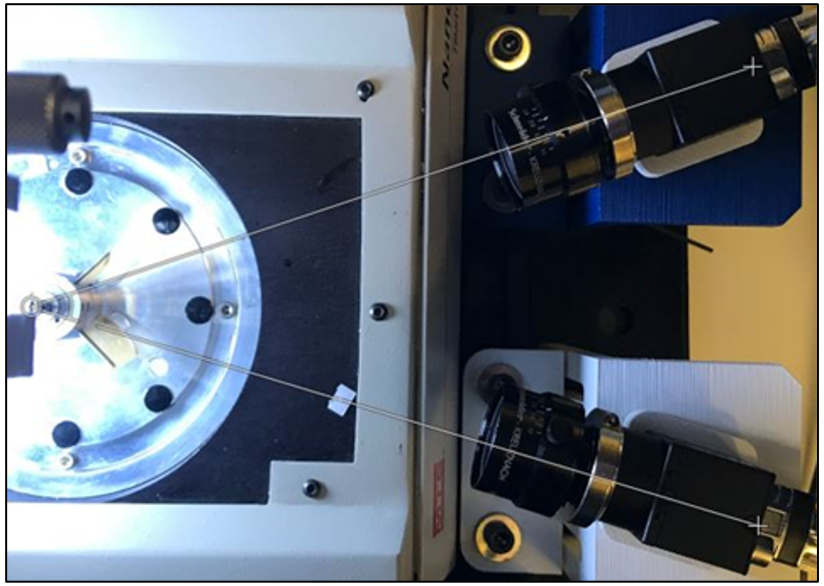


Tensile modulus of Zoltek PX35 CFs
(10.5% modulus reduction for 10° offset, N = 35 samples, 99.5% confidence interval)

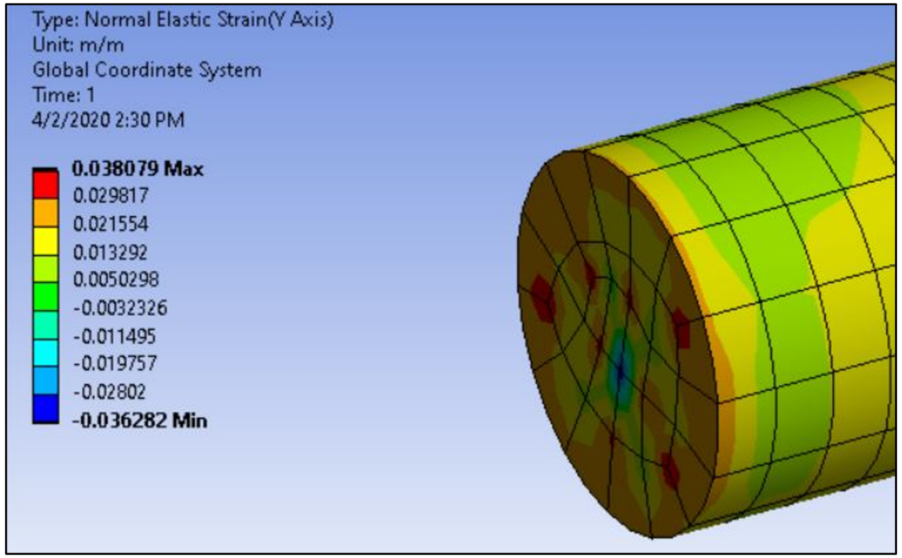
Optical Off-Axis Alignment Setup



Fiber mounted at 10° offset in tensile tester (UVa).



Custom stereovision system designed to measure offset angle of fibers during tensile testing (UVa).



Finite element analysis currently being used to validate experimental results (UVa).

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Any proposed future work is subject to change based on funding levels.